AD-A281 570

**ATION PAGE**

average 1 hour per response, including the time for reviewing instructions, searching existing data sources,
ng the collection of information. Send comments regarding this burden estimate or any other aspect of this
to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson
of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503

| | | |
|---|---|---|
| **ATE** 7/8/94 | **3. REPORT TYPE AND DATES COVERED** 1/1/93 – 7/8/94 | |

| **4. TITLE AND SUBTITLE** NMR Studies of Polymers at Interfaces | **5. FUNDING NUMBERS** PE-N0014-91 PR-1274 |
|---|---|
| **6. AUTHOR(S)** Frank D. Blum | |

DTIC
SELECTE
JUL 15 1994
B
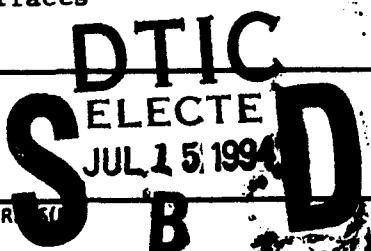
| **7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)** University of Missouri-Rolla Department of Chemistry Rolla, MO 65401 ATTN: Frank D. Blum | **8. PERFORMING ORGANIZATION REPORT NUMBER** UMR-FDB- 41 |
|---|---|
| **9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)** Office of Naval Research - Code 5000 Chemistry Division 800 Quincy Street Arlington, VA 22217 ATTN: Kenneth J. Wynne | **10. SPONSORING/MONITORING AGENCY REPORT NUMBER** |

**11. SUPPLEMENTARY NOTES**

| **12a. DISTRIBUTION/AVAILABILITY STATEMENT** Unlimited - Approved for unlimited public release | **12b. DISTRIBUTION CODE** |
|---|---|

94-21519

**13. ABSTRACT** *(Maximum 200 words)*

A review of NMR studies done in our laboratory on the dynamics of polymers adsorbed at interfaces is made. Of specific interest is polymers adsorbed on solid substrates at the (i) solution, (ii) gas, and (iii) polymer interface. In solution we have used deuterium NMR relaxation times to show the enhanced motional mobility of styrene segments of vinylpyridine-styrene block copolymers, adsorbed on silica, and swollen with toluene. At the gas interface, we show how the presence of the interface can turn a rubbery polymer into a glassy one with carbon-13 studies of poly(*iso*-propyl acrylate). At the polymer interface, we show how the overpolymerization of bismaleimide slows the dynamics of the interfacial layer of silane coupling agent.

DTIC QUALITY INSPECTED 8

| **14. SUBJECT TERMS** Polymers, Interfaces, NMR, Surfaces | **15. NUMBER OF PAGES** 6 |
|---|---|
| | **16. PRICE CODE** |

| **17. SECURITY CLASSIFICATION OF REPORT** Unclassified | **18. SECURITY CLASSIFICATION OF THIS PAGE** Unclassified | **19. SECURITY CLASSIFICATION OF ABSTRACT** Unclassified | **20. LIMITATION OF ABSTRACT** |
|---|---|---|---|

NSN 7540-01-280-5500

94 7 12 083

OFFICE OF NAVAL RESEARCH

Grant N00014-91-J-1274

R&T Code 413m005---04

Technical Report # UMR-FDB-41

NMR Studies of Polymers at Interfaces

by

Frank D. Blum

Department of Chemistry and Materials Research Center
University of Missouri-Rolla
Rolla, MO 65401

(314) 341-4451

Prepared for Publication in

*Polymeric Materials Science and Engineering*

July 8, 1994

# NMR Studies of Polymers at Interfaces

Frank D. Blum
Department of Chemistry and Materials Research Center
University of Missouri-Rolla
Rolla, MO 65401

## INTRODUCTION

Polymers are usually used in applications with other materials as a filler, fiber or matrix. These systems may be diverse and span a broad range of applications. The ultimate properties of such systems depend not only on the bulk properties of the components, but also on how they interact. This interaction chiefly occurs through an interfacial layer between the two bulk materials. Unfortunately, the interfacial material is difficult to study because it is often so thin.

Thin films are not easy to study with macroscopic techniques, but are often reasonable to study with microscopic ones. Many of the microscopic techniques require a clear sample to probe them or their use limits analysis to the outer surface. NMR does not suffer from this limitation and can be used on opaque materials. Unfortunately, it does suffer from relatively low sensitivity. In order to cope with this low sensitivity, high surface area materials must be used.

In this paper, the results of several studies performed in our laboratory on interfacial materials using NMR techniques are discussed. Specifically, the focus is on the dynamics of interfacial species, attached to solid substrates, at the solid-liquid, solid-gas, and solid-polymer interface. The application of NMR to problems of interfacial polymers [1], thin organic films [2], and the use of NMR-active isotopes at interfaces [3] have been reviewed by the author.

## EXPERIMENTAL

The spectra shown and discussed below were mostly taken on a Varian VXR-200 NMR spectrometer nominally operating at 200 MHz for protons, 50 MHz for $^{13}C$, and 31 MHz for $^2H$. The $^{13}C$ solid spectra were taken with magic-angle spinning (MAS) and high-power proton decoupling (DD). The solid-state deuterium spectra were taken with a quadrupole echo with an alternate 180° pulses (SSECHA) and the appropriate phase cycling to reduce coherent noise. High power pulses (2µs for 90°) and fast digitization was also used. Liquids spectra and relaxation times were taken with standard equipment and pulsed techniques.

## RESULTS AND DISCUSSION

In order to illustrate some of the possible applications of NMR to polymeric materials at interfaces, we examine three different situations where the adsorbates are located at different interfaces. The scope will be restricted to adsorbates on solid surfaces.

## Solid-Liquid Interface

Polymers are now being designed for optimum performance as stabilizers. Block copolymers may be useful as compatabilizers or as interfacial agents. An interesting system is blocky poly(styrene-co-2-vinylpyridine) (VPS) adsorbed on silica. In this system, the vinylpyridine adsorbs to silica much more strongly than styrene. In this self-assembling system, the 2-vinylpyridine (VP) segments may be considered to be terminally attached and the styrene (S) segments may be extended away from the surface.

In order to probe the dynamics of these polymers, two terpolymers were prepared [4] with deuterium atoms selectively placed on the styrene methine. They were polymerized in a blocky fashion by sequential addition with anionic polymerization. These polymers are labelled VPDSS and VPSDS where DS and S distinguish deuterostyrene from styrene, respectively.

$$(CH_2CH)_x \cdot (CH_2CD)_y \cdot (CH_2CH)_z \qquad (CH_2CH)_x \cdot (CH_2CH)_y \cdot (CH_2CD)_z$$
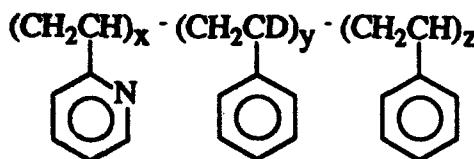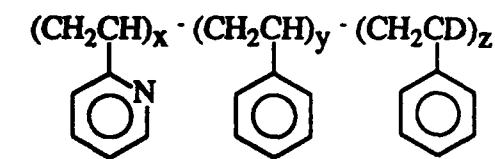
**VPDSS**                                    **VPSDS**

Both polymers were polymerized to molecular weights of about $M_w = 20,000$ g/mol with polydispersities of 1.4-1.5. The values of x, y, and z were such that the polymers were 25 % VP, 37.5% DS, and 37.5%S. The polymers were adsorbed onto silica surfaces (Cab-O-Sil, grade M-5, surface area 200 m$^2$/g) from toluene and carbontetrachloride.

$^{13}C$ NMR spectra gave a strong indication of differences between the VPS polymer in solution and that adsorbed on silica, both diluted with toluene. In the solution case, all resonances for both parts of the polymer were narrow and resolved, indicative of rapid motion of the segments. In contrast, on the surface, but swollen with toluene, only the styrene resonances were observed. The VP resonances were broadened because of their interaction, and relative immobility, with the surface. Thus the spectra were consistent with the notion of the polymer being bound through the VP segments.

Deuterium NMR relaxation times $T_1$ and $T_2$ of the backbone deuteron of the polymers have also been measured in different solvents. The liquid-like resonance was found to be adequately described by a single exponential decay constant. Some results of these measurements are found in Table I. While there are more quantitative ways to interpret the relaxation time measurements [4,5], we have found that the $T_1/T_2$ ratio is a good measure of the relative mobility of the polymer.

The relaxation data for the two polymers (VPDSS vs VPSDS), swollen with the same solvent, are similar in magnitude for each case. Slightly longer relaxation times are found in the VPSDS where the deuterated

segments are further away from the point of attachment (VP) to the surface. In this regime, a longer relaxation time is indicative of less restricted motion. Comparison of the results for the same polymer in different solvents reveals that the relaxation times are lengthened as the solvent quality increases, also suggesting less restricted motion in good solvents. The ratios of the relaxation times shown in the table are smallest for the good solvent, toluene. Surprisingly, the ratio for the surface-bound polymers in toluene is even less than that for the polymers in solution. This is consistent with the notion that the mobility of the styrene segments on the surface, swollen in toluene, is greater than that in solution. This is at first a surprising result, but is probably due to very different segment-segment interactions in solution and in stretched out chains.

**Table I.** Relaxation data for VPDSS and VPSDS on silica in different solvents at 18 °C.

| SYSTEM | SOLVENT | $T_1$(ms) | $T_2$(ms) | $T_1/T_2$ |
|--------|---------|-----------|-----------|-----------|
| VPDSS | toluene | 3.63 | 3.38 | 1.07 |
| | $CCl_4/CH_3OH$ | 3.34 | 2.05 | 1.63 |
| | $CCl_4$ | 3.05 | 1.80 | 1.69 |
| | toluene solution* | 3.63 | 2.75 | 1.32 |
| VPSDS | toluene | 3.94 | 3.60 | 1.09 |
| | $CCl_4/CH_3OH$ | 3.49 | 2.76 | 1.26 |
| | $CCl_4$ | 2.97 | 1.92 | 1.55 |
| | toluene solution* | 3.94 | 3.25 | 1.21 |

*Interpolated to the same $T_1$ value as for the surface/toluene system.

Thus for the surface-bound polymers the picture that emerges is one of highly extended, rapidly moving polymer segments when swollen with toluene. In the presence of the other solvents, the polymer segments maybe somewhat extended, but not as extended as in toluene. Their molecular motion is also significantly reduced compared to that in toluene. The relative mobility of the styrene segments is dependent on the solvent quality.

**Solid-Gas Interface**

The mobility of a polymer adsorbed on a solid surface has been probed indirectly with ^{13}C NMR using magic-angle spinning and dipolar (high-power proton) decoupling. Poly(*iso*-propyl acrylate) (PiPA) was chosen for these studies because it is a flexible polymer and above its glass transition temperature under ambient conditions. Shown in Figure 1 are the MAS-DD spectra of the bulk polymer and that adsorbed at monolayer coverage on silica [6]. In bulk, the spectrum shows only the resonances from the side-chain carbonyl and methyl groups, with only a hint of the side chain methine. In contrast, the monolayer-surface spectrum shows resolved resonances for all of the carbons expected.

While it is not always possible to reproduce this startling contrast in bulk and surface species, there are some important lessons to be learned from this system. PiPA at room temperature is a flexible polymer which undergoes motion in the KHz range. This is the within frequency range of both the magic-angle spinning and also the dipolar decoupling. Incoherent motions in this frequency range can *undo* the coherent averaging of either the MAS or DD. On the surface, these motions are effectively slowed down and out of the operative range for MAS or DD. Consequently, the coherent averaging can take place, resulting in a resolved set of resonances. These are very similar to those obtained from a glassy polymer like poly(methyl methacrylate). It is therefore concluded that the presence of the surface has the effect of transforming the PiPA from rubbery to glassy at room temperature. From observations of the broadening as a function of surface coverage, a rough distance scale over which this interaction is effective was estimated to be about a single monolayer. The dynamics of the interfacial polymer increases as the distance away from the surface increases.
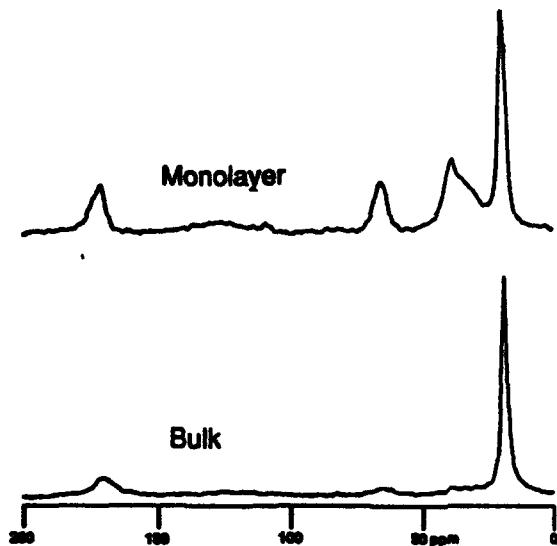


Figure 1. $^{13}C$ MAS spectrum of PiPA in bulk (bottom) and at monolayer coverage (top) on silica.

## Solid-Polymer Interface

Our work on the interface in composite materials has also shown us how to probe the interfacial species in the presence of overlayers of polymer. We have used deuterium labelling to provide the necessary contrast. Silane coupling agents which were deuterated next to the nitrogen were prepared:

$(X)_3\text{-Si-}(CH_2)_2CD_2NH_2$                $(X)_3\text{-Si-}(CH_2)_3CD_2NH_2$

**DAPS**                                    **DABS**

These materials differed mainly in their chain length which resulted in differences in dynamics of the chains. At the silica interface, the initial monolayer is relatively rigid and as multilayers are formed, the crosslinked material becomes more flexible [7]. Ultimately, for the bulk cross-linked polymer, DABS moves about 10 times faster than the DAPS. This graded interface may be one of the reasons (in addition to chemical bonding) why these coupling agents work so well in composite materials. Shown in Figure 2 is the deuterium NMR solid-state spectrum of DABS adsorbed in monolayer coverage on silica. In the upper spectrum, the same material that has been overpolymerized with bismaleimide (BMI) is shown. The broader spectrum for the material with the polymer overlayer is indicative of (i) a change in the mechanism, and (ii) a decrease in the rate of motion of the DABS. The coupling agent becomes somewhat *locked in* with overpolymerization with BMI because of its interaction with the polymer.
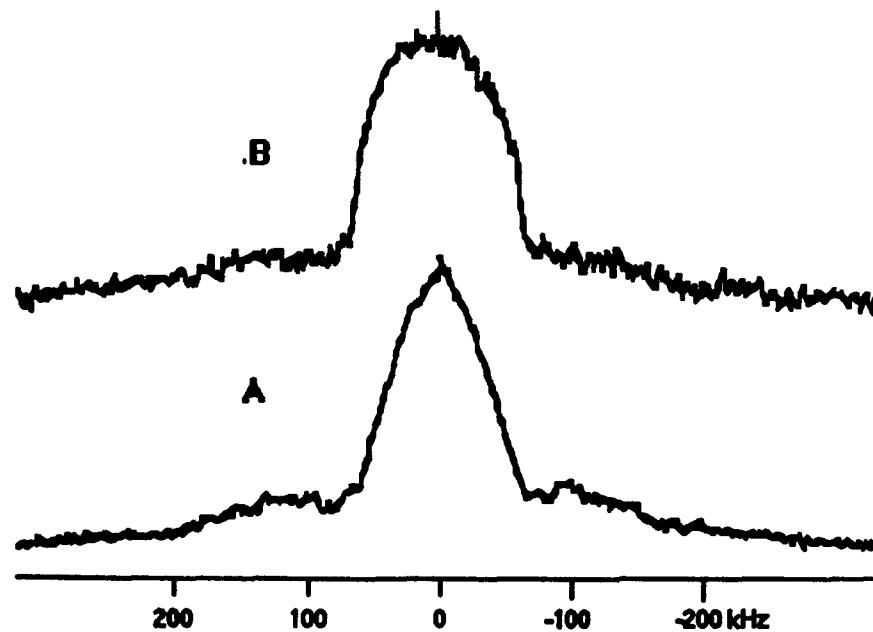


Fig. 2. Deuterium NMR spectra DABS at (A) monolayer coverage alone and (B) monolayer coverage, overpolymerized with bismaleimide. (after Ref. 8)

## CONCLUSIONS

NMR has the sensitivity to probe interfacial material on high surface area substrates. The results may be used to aid our understanding of the structural and dynamic properties of the interfacial material. These studies should be useful in their application in the design of new interfacially active species which can enhance the properties of new materials.

## ACKNOWLEDGEMENT

## REFERENCES and NOTES

1. F.D. Blum, *Colloids and Surfaces*, **45**, 361-376 (1990).
2. F.D. Blum, Annual Reviews of NMR Spectroscopy, G. Webb, ed., Academic Press, London, UK, in Press.
3. F.D. Blum, Characterization of Composite Materials, H. Ishida, ed., Manning Publications, Greenwich, CT, in Press.
4. F.D. Blum, B.R. Sinha, F.C. Schwab, *Macromolecules*, **23**, 3592-3598 (1990).
5. B.R. Sinha, F.D. Blum, and F.C. Schwab, *Macromolecules*, **26**, 7053-7057 (1993).
6. F.D. Blum, R.B. Funchess, W. Meesiri, in Solid State NMR of Polymers, L. Mathias, Ed., Plenum Press, New York, 1991, p271-281.
7. H.-J. Kang and F.D. Blum, *J. Phys. Chem.*, **95**, 9391-9396 (1991).
8. J.E. Gambogi and F.D. Blum, *Macromolecules*, **25**, 4526-4534 (1992).